P. R. MALLORY & CO. INC.

CORPORATE CHEMICAL LABORATORY

CELL EQUALIZATION TECHNIQUES

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FOREWORD

This report was prepared by P. R. Mallory & Co. Inc., Indianapolis, Indiana for Aeronautical Systems Division of Wright-Patterson Air Force Base, Ohio, on Contract Number AF 33(657)-8749, Task 817304-18. It is our pleasure to acknowledge the assistance of Mr. W. S. Bishop of the Aeronautical Systems Division, who is the project engineer.

The work covered by this report was accomplished under Air Force Contract No. AF 33(657)-8749, but is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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ABSTRACT

Additional work on the 1.5 volt nickel-cadmium cell stabistor and experimental test results verify the feasibility of equalising the cells of a series connected group by use of stabistors.

Effort was directed toward the design of a 2.0 volt stabistor for use with the silver-zinc couple. Preliminary theoretical and experimental investigations indicate satisfactory operation of the stabistor on the lower voltage plateau; operation on the higher voltage plateau is expected to involve severe losses.

The specific voltage of the anti-reversal device has been reduced by about 10% by a different method of junction formation.

One experimental charge control circuit has been cycled in excess of 1250 times and a second circuit was cycled 785 times without catastrophic failure of cells or semiconductors.

I. INTRODUCTION

The space vehicle power supply requisites of reliability and unattended operation capability are presently most nearly fulfilled by the solar cell-alkaline battery system. In earth satellite applications this energy conversion system may operate in a cyclic manner, the solar cells delivering power to the batteries and the batteries in turn delivering power to the load during respective light and dark portions of the orbit. Required battery voltages are obtained by series connection of a suitable number of individual cells. In the interest of weight and physical dimensions the removal and reinsertion of an appreciable part of the battery capacity during a given orbit is indicated.

Solar cell current is nearly constant over a relatively wide voltage range and constant current charging of the alkaline battery is appropriate. Due to inherent differences in cell capacity and internal resistance, the instantaneous cell terminal voltages of a battery being charged by constant current are generally unequal, inferior cells reaching maximum terminal voltage ahead of cell having higher capacity and lower internal resistance. During discharge, any cell of the battery, not capable of discharging at the rate set by the remaining cells and the load will be forced into voltage reversal and effectively reverse charged. Either condition can lead to electrode degeneration and electrolyte decomposition. Extensive electrolyte decomposition is, of course, intolerable in the sealed space cell.

The P. R. Mallory Company submitted to Aeronautical Systems Division a proposal entitled "Cell Equalization and Anti-Cell Reversal Techniques for Secondary Batteries" in response to Purchase Request No. 127425 and as a result was awarded Contract AF 33(657)-8749 effective 1 October 1962 and terminating 30 September 1963. One objective of this program is to investigate methods of equalizing the terminal voltage of individual secondary cells in a series connected group. Another objective is to investigate methods of preventing cell reversal upon discharge. The work program will include, but will not be limited to theoretical and experimental determination of a reliable method of cell equalization on charge and elimination of cell reversal on discharge. It will also embrace applied research on the equalizer and anti-reversal semiconductor devices with sufficient evaluations to determine that the method is reliable and practical. Two experimental sets including batteries shall be delivered.

II. DISCUSSIONS AND FACTUAL DATA

A. Semiconductor Material and Device Study

1. General:

During the third quarter of the contract additional work was done on the 1.5 volt nickel-cadmium cell stabistor and effort was directed toward the design of a 2.0 volt stabistor for use with the silver zinc couple. Larger, more planar junctions were alloyed in germanium resulting in anti-reversal devices of improved characteristics.

2. The Nickel-Cadmium System Equalizer:

The nominal limiting 1.5 volts, characteristic of the nickel-cadmium system can be obtained, as reported previously, by use of two forward biased junctions in silicon. The stabistor is described by equation (1), in which the terms have the usual meaning, over the operating range of interest.

$$J = J_o \frac{qV}{NKT} \qquad (1)$$

Since the junctions are bonded together in series, the compensation term N must be assigned values ranging from 2 to 4. The incremental conductance of the junction is given by the derivative of equation (1).

$$\frac{dJ}{dV} = \frac{q}{NKT} J = g \qquad (2)$$

Where g is the incremental conductance per unit junction area. The N term can be eliminated between equations (1) and (2) as shown by equation (3).

$$Vg = J \ln \frac{J}{J_o} \qquad (3)$$

and

$$VgA = I \ln \frac{J}{J_o}$$

where A = junction area

I = junction current (amp)

In the case of the 3.2 ampere hour cell, operated to 75% discharge depth in the 90 minute cycle, the charge and discharge currents are 3.4 and 4.12 amperes respectively. Let it be assumed that at the end of charge the stabistor voltage and current are 1.48 volts and 1.0 ampere (30% of the charge current) for a normal cell and 1.52 volts and 3.4 amperes in the worst case. The slope of the required characteristic is therefore 60 (amperes/volt) at the operating point. The voltage and slope requirements should be met, according to equation (4), when the ratio $\frac{J}{J_o}$ is equal to 3×10^{11}. Assuming worst case junction current density of about 150 amp/in^2, the use of 0.01 ohm-cm p type silicon, processed as previously described, will result in such a ratio at room temperature.

The above discussion was oversimplified in that the temperature sensitivity of the saturation density was not given due consideration. In operation, the cell stabistor is subject to a positive bias (the cell terminal voltage) which increases from about 1.3 to 1.5 volts in 55 minutes The skirts of the plateau like regions of the charge characteristic are soft enough that the stabistor is virtually in thermal equilibrium at all times. In fact, to track the cell temperature, which varies considerably over a given cycle, the stabistor and cell must be thermally connected through a low impedance path. As the stabistor current slowly increases, the saturation density increases at a faster rate because, in part, of self heating. In other words, the ratio J/J_o, and thus $\ln J/J_o$, is an inverse function of temperature.

The junction saturation density in the 0.01 p type silicon, processed as described previously, increases by a factor of about 30 as junction temperature increases from 75F to 150F while that in 0.005 ohm-cm p type silicon junction increases only about 7 times over the same temperature excursion. To comply with the cell temperature coefficient, the 0.005 ohm-cm material must be utilized at the cost of a very slight decrease in slope of the device characteristic.

3. The Silver-Zinc System Equalizer:

The silver-zinc system limiting charge voltage has been established[1, 2] as about 1.97-1.99 volts under room temperature conditions. The charge voltage characteristic is distinguished by two plateaus as shown by Figure 1 which is a plot of data obtained during the charging of a typical 25 ampere hour cell at constant 1.5 amperes. Figure 2 shows terminal voltage of the same cell over one 90 minute cycle. Starting at full charge, in this case, the cell was discharged 35 minutes at constant 10.7 amperes then recharged 55 minutes at constant 6.8 amperes.

Referring to Figure 1, three modes of cell operation are possible. They are: (a) Operation within the 1.60-1.64 volt level, (b) Operation within the 1.92-1.99 volt level, and (c) Operation within both levels. Only modes (a) and (b) need be considered with respect to equalization, since a stabistor suitable for (b) would also be suitable for (c).

(a) Lower Level Operation:

Referring again to Figure 1, the conductance of the stabistor, if the stabistor-cell pair is to operate on the lower plateau, must be as shown by equation (5).

$$g \geqq 4I \quad \text{(mhos)} \qquad (5)$$

where I is the nominal constant charge current required without the stabistor. The current input to the circuit must be increased sufficiently to compensate the losses. This increase is approximately the stabistor current at 1.64 volts. The slope and voltage requirements can be met by use of either two silicon junctions operating between about 100 and 1100 amps/in^2, or two silicon and one germanium junctions operating between the limits of about 10 and 110 amp/in^2. The device efficiency is about 90% in both cases.

(b) Upper Level Operation:

By the reasoning previously employed, the conductance of the stabistor, operated with the cell on the upper plateau, should be as given by equation (6)

$$g \geqq \frac{I}{1.97-1.92} = 20I \quad \text{(mhos)} \qquad (6)$$

where I is again the nominal cell charge current required without the stabistor. According to equation (2), such a value of conductance is impossible for a compound three junction structure since it requires that N equal 2 at room temperature. In fact, equation (2) predicts that the conductance of any three junction structure will be no greater than 13.3 I at room temperature. Operation of the stabistor on the upper plateau will therefore be costly in terms of the additional charge current required.

The limiting 1.99 volts at specified currents can be obtained, while maintaining reasonable junction areas, by stacking three junctions in very low resistivity (0.0005 ohm-cm p type) silicon or by stacking two higher resistivity silicon and one germanium dice. In practice, considerably steeper V-I curve slopes and parameter uniformity have resulted from the silicon-germanium combination, however, some difficulty has been encountered in obtaining a mechanically strong bond at the silicon germanium surfaces.

4. Junctions in Germanium:

In germanium, penetration and area control are critical aspects of the alloying process. Both are dependent, in part, on time in and temperature of the heat zone, and on the pressure of the alloying agent against the germanium dice. Electrical (and mechanical) properties of the junction are dependent, in part, on heating and cooling rates. After considerable experimentation involving the above variables, the following method of fabrication of germanium junctions acceptable to the stabistor requirements has evolved. Germanium dice are sandwiched between tin gallium and tin antimony preforms and held in place by a weight of about 10 oz/in^2 of preform area. This assembly is heated to 600°C and held at 600°C for five minutes, cooled to 400°C then removed from the furnace. Heating rate is 20°C/minute; cooling rate (600°C to 400°C) is 10°C/minute. The furnace atmosphere is hydrogen. Planar junctions 1 mil deep are consistently obtained and electrical characteristics are uniform. The surfaces of such dice can readily be bonded to the gold plated silicon dice.

Reduction of the anti-reversal device specific voltage has been accomplished by alloying as described above over previously diffused junctions in germanium. Figure 3 shows typical volt-density curves characteristic of the two processes.

B. Prototype Device Fabrication and Evaluation

1. General:

During this quarter testing of the experimental charge control circuits was continued. Additional stabistors and anti-reversal devices were fabricated and evaluated. Environmental testing of sample devices was initiated.

2. Experimental Charge Control Circuit Testing:

Circuit BCC-2, discussed in the last report, has completed more than 1250 cycles at ASD. The test is being continued. Early in the test it was determined that unsatisfactory operation resulted when part of the cells were protected and part not protected. The unprotected cells were then removed and the test continued.

Circuit BCC-3, in which series connected groups of two paralleled semiconductor sets each were used, was operated 785 cycles, with no failures of cells or protective devices, then discontinued. One set of cells reversed 14 consecutive times during the first 100 cycles, then apparently recovered and completed the test without additional reversals. During preliminary testing at constant current, the currents of the paralleled cells, in some cases, became grossly unequal during the last few minutes of charge and discharge. This effect is less pronounced in the constant load mode of operation.

The stabistor and anti-reversal diode pairs were approximately rather than rigorously matched when selected and the maximum observed hogging of current was by a 1.90/1.35 ratio which could be improved by more careful selection of units. Temperature behavior of the cells was similar to that of cells in the second circuit.

A brief summary of third and 785th cycle data is shown by the following table.

TABLE I

	3rd Cycle			785th Cycle		
Group	1	2	3	1	2	3
End of Charge Voltage	1.50	1.49	1.50	1.50	1.50	1.50
Equalizer Amperes	2.19	1.60	1.79	3.78	3.08	3.25
Temperature (F)	105	105	103	113	111	110
End of Discharge Voltage	1.15	1.02*	1.16	0.980	0.965	1.09
Temperature	99	103	100	100	100	99

*Reversed before measurements were completed.

Environmental testing of sample units has been initiated and results will be included in the final report. The thermal resistance of the two junction nickel-cadmium cell stabistor has been determine as 1.2°C/watt; that of the three junction silver-zinc cell stabistor as 5°C/watt, both with respect to the heat sink. Thermal resistance of the silver-zinc cell stabistor is considerably higher than anticipated and must be reduced.

III. PROGRAM FOR NEXT INTERVAL

1. Testing of the sealed alkaline cells will be continued.
2. Environmental testing will be continued.
3. The experimental hardware sets will be constructed.

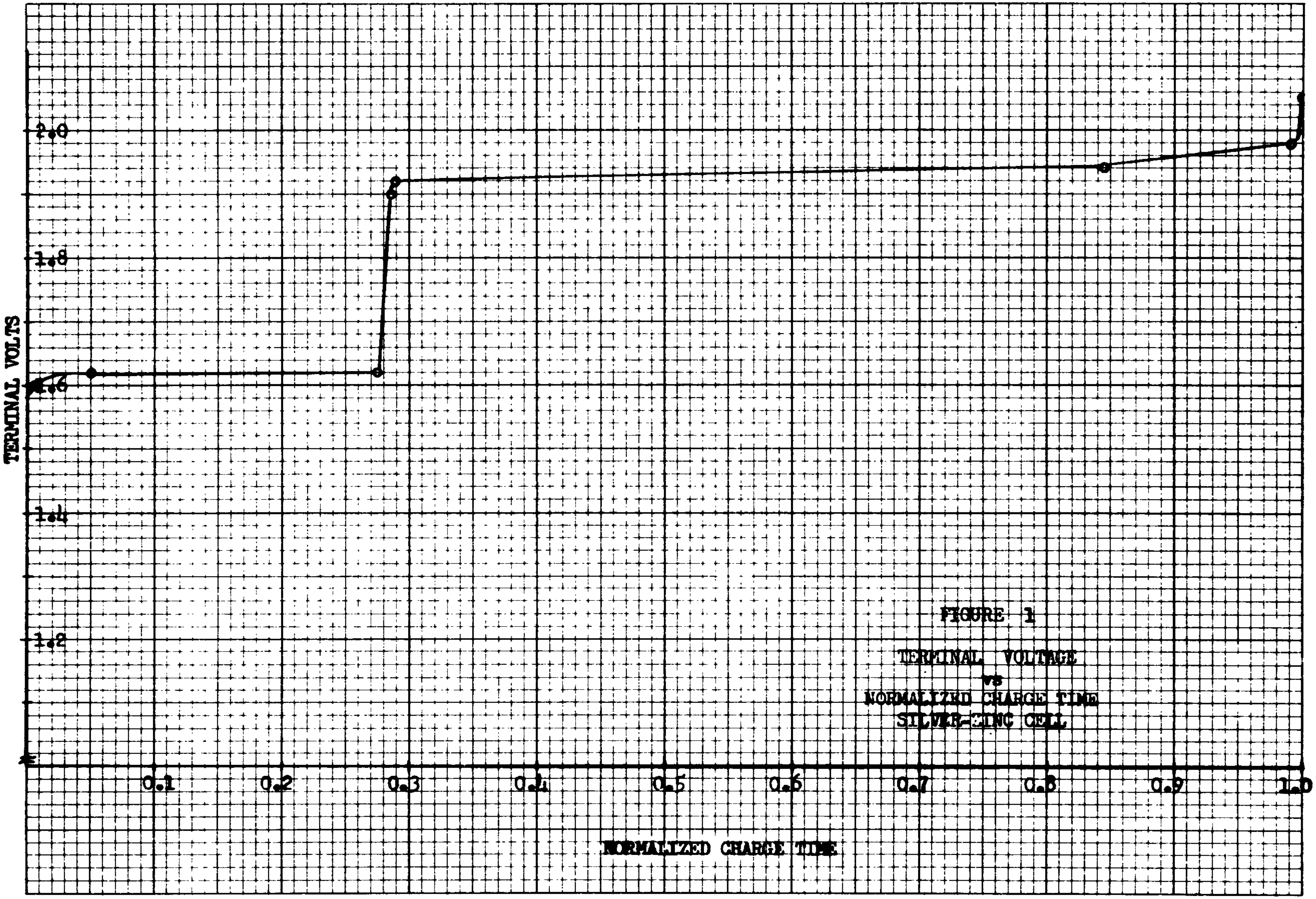


FIGURE 1

TERMINAL VOLTAGE
vs
NORMALIZED CHARGE TIME
SILVER-ZINC CELL

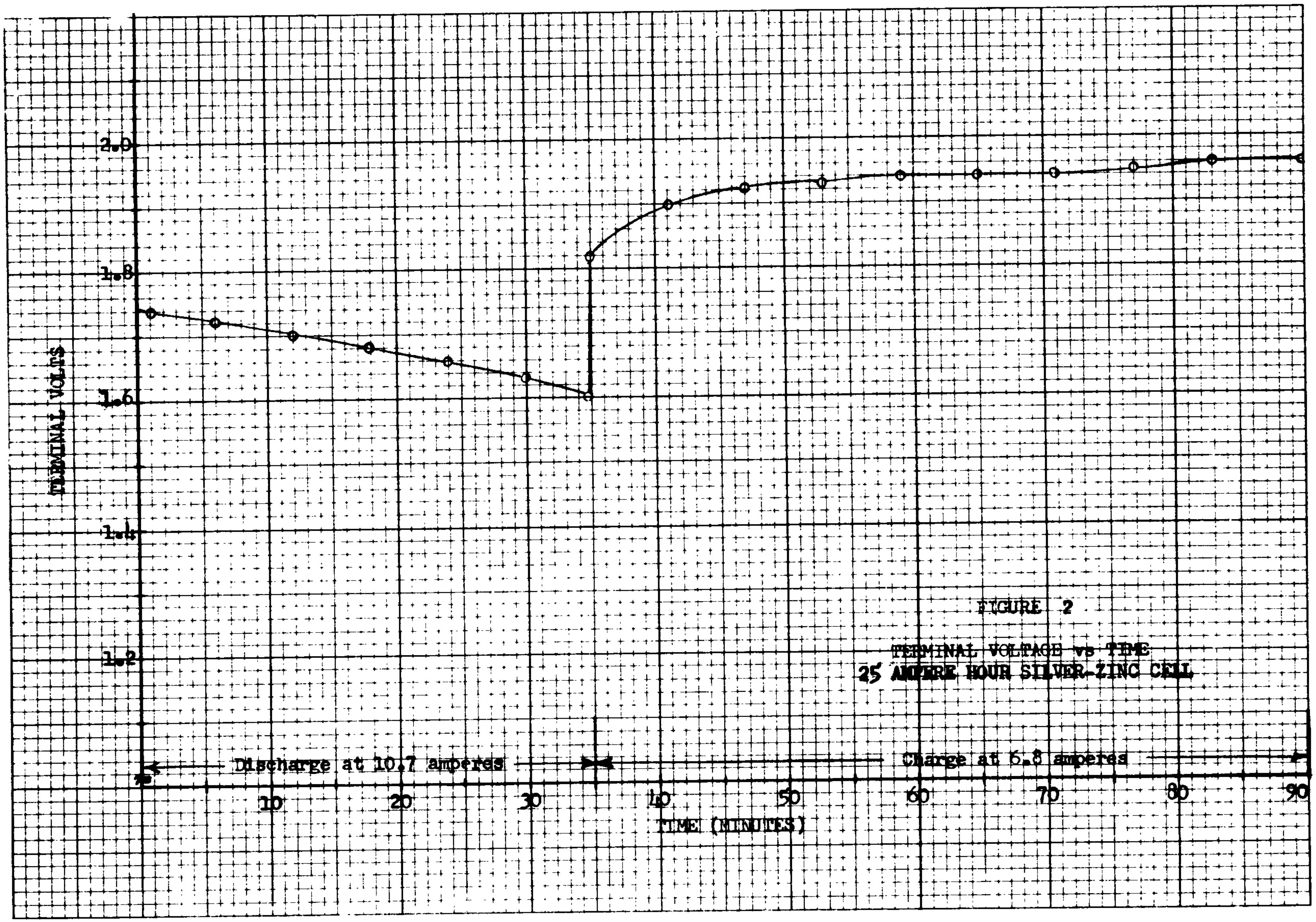
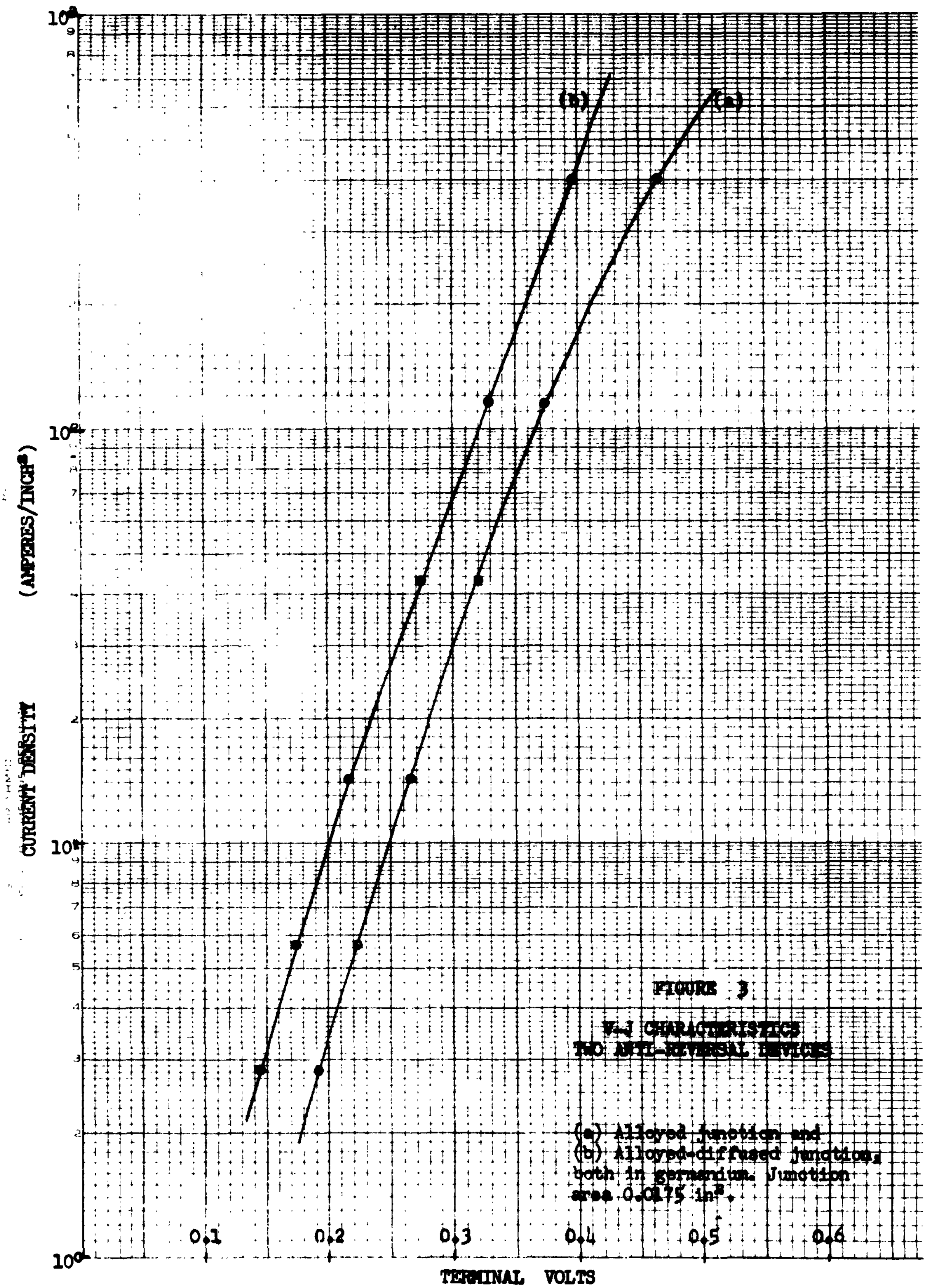


FIGURE 2

TERMINAL VOLTAGE vs TIME
25 AMPERE HOUR SILVER-ZINC CELL



CURRENT DENSITY (AMPERES/INCH²)
TERMINAL VOLTS
0.1
0.2
0.3
0.4
0.5
0.6
(b)
(a)
FIGURE 3
V-J CHARACTERISTICS
TWO ANTI-REVERSAL DEVICES
(a) Alloyed junction and
(b) Alloyed-diffused junction,
both in germanium. Junction
area 0.0175 in².

REFERENCES:

1. W. W. Clark, W. G. Ingling, I. F. Luke, R. Leaf, "Alkaline Battery Evaluation", ASD-TDR-62-893, October 1962.

2. I. F. Luke, Inland Testing Laboratories, Dayton, Ohio, letter dated 4 December 1962.

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